Photoproduction of Hydrated Electron from Constituents of Natural Waters

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The wavelength dependence for the photoproduction of the hydrated electron ($e^-_{(aq)}$) from various humic and fulvic acids and from natural waters was determined, employing a method that converts $e^-_{(aq)}$ to a methyl radical that is detected fluorimetrically as the *O*-methylhydroxylamine of a stable nitroxide. Quantum yields for $e^-_{(aq)}$ production from potassium ferrocyanide and *N,N*-dimethylaniline are in agreement with previously reported values. The quantum yields for production of $e^-_{(aq)}$ from colored dissolved organic matter (CDOM) decrease precipitously with increasing wavelength with the rate of decline increasing in the order: humic acid < fulvic acid < natural water in the UV-B region. For Suwannee River fulvic acid, quantum yields ranged from 7.9×10^{-6} at 366 nm to 1.9×10^{-4} at 296 nm indicating that previously reported values for $e^-_{(aq)}$ production from CDOM involving laser sources of irradiation are high due to experimental artifact. Apparent natural water quantum yields at 296 nm are higher than those for humic substances, ranging from 9.4×10^{-5} to 3.7×10^{-3} depending on location. The highly absorbing waters of the Delaware and Chesapeake Bays show insignificant production of $e^-_{(aq)}$. These results indicate that the hydrated electron, through its reaction with dioxygen, is not a significant source of hydrogen peroxide in many natural waters and that humic substances may not be the principal source of $e^-_{(aq)}$ production.
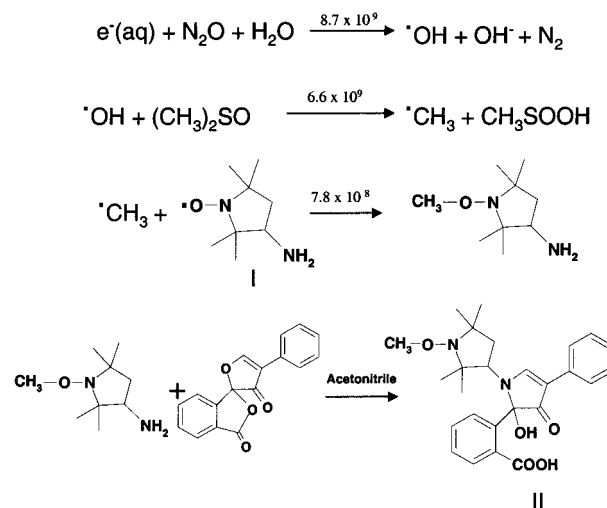
Introduction

The hydrated electron ($e^-_{(aq)}$) is a highly reactive, strongly reducing species, which has been previously reported to be produced upon the photolysis of colored dissolved organic matter (CDOM) in natural waters and in solutions of humic substances (*1–3*). The hydrated electron can affect the redox chemistry of natural waters either through the formation of H_2O_2 (rxns 1–2) or through the direct reductive dehalogenation of organic pollutants bound to CDOM (*4, 5*).

$$e^-_{(aq)} + O_2 \rightarrow O_2^- \qquad (1)$$

$$2O_2^- + 2H_3O^+ \rightarrow H_2O_2 + O_2 + 2H_2O \qquad (2)$$
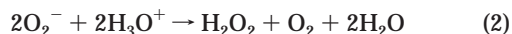
To evaluate quantitatively the potential importance of $e^-_{(aq)}$ as a source of H_2O_2 in natural waters and its effect on pollutant transformation, the efficiency of its production (i.e., quantum yield) at environmentally relevant wavelengths is

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SCHEME 1

needed. Although past laser flash photolysis (LFP) studies have provided evidence for the photoproduction of $e^-_{(aq)}$ from humic substances and in natural waters (*1–3*), the wavelength dependence of this production has yet to be determined. Moreover, quantum yields determined through the use of LFP were found to be 2 orders of magnitude higher than those acquired using low intensity, continuous irradiation and 2-chloroethanol as a probe (*3*). Two explanations have been put forward to explain this discrepancy. The first suggests that the higher yields of $e^-_{(aq)}$ obtained in LFP experiments are due to biphotonic processes and thus are environmentally irrelevant. The second argues that the 2-chloroethanol probe employed in the steady-state irradiations did not completely scavenge $e^-_{(aq)}$ due to the rapid loss of this species through recombination within the humic substance.

Here we describe a simple, highly sensitive approach that can be used to independently quantify the photoproduction of $e^-_{(aq)}$ by humic substances. This approach uses two methods with differing reaction schemes for $e^-_{(aq)}$ detection. One method employs the reaction of $e^-_{(aq)}$ with nitrous oxide (N_2O) (rate constant 8.7×10^9 M^{-1} s^{-1}, ref *6*) to produce a hydroxyl radical (•OH), which upon reaction with dimethyl sulfoxide generates a methyl radical. This methyl radical is trapped with 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy free radical (**I**) and quantified fluorimetrically as the *O*-methylhydroxylamine (**II**) following derivatization with fluorescamine (see Scheme 1, and ref *7–9*). The second method employs the reaction of $e^-_{(aq)}$ with chloromethane (CH_3Cl) to produce the methyl radical directly (rxn 3); the methyl radical is then trapped by **I**, with **II**, then analyzed as described above.

$$CH_3Cl + e^-_{(aq)} \rightarrow CH_3 + Cl^- \qquad (3)$$
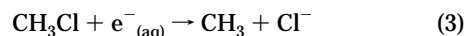
To establish that these methods provided accurate quantification of $e^-_{(aq)}$ production, potassium ferrocyanide and *N,N*-dimethylaniline (DMA), compounds that are known to produce $e^-_{(aq)}$ in high yield (*10, 11*), were first examined. Subsequent application of these methods to solutions of humic substances and natural waters reveals that the quantum yields for $e^-_{(aq)}$ production are far lower than those previously reported in LFP studies, suggesting that the high yields observed in those studies were an artifact, possibly

due to biphotonic processes. Significant variations in the wavelength dependence and magnitude of $e^-_{(aq)}$ production were observed between the humic substances and some natural waters, indicating that in certain natural waters, humic substances are not always the principal source of $e^-_{(aq)}$.

Experimental Section

Materials. Boric acid (99.999%), potassium ferrocyanide (II) trihydrate (99%), *N,N*-dimethylaniline (DMA, 99.5%), dimethyl sulfoxide (DMSO, 99.9%), and sodium hydroxide were obtained from Aldrich; 3-amino-2,2,5,5 tetramethyl-1-pyrrolidinyloxy free radical (**I**, 99%, Acros), potassium nitrite, sodium nitrate, methanol (HPLC grade), and glacial acetic acid were obtained from Fisher. Acetonitrile (HPLC grade) was obtained either from Fisher or Aldrich, while fluorescamine was obtained from Sigma. Argon (ultrahigh purity) and N_2 were obtained from Air Products, CH_3Cl (99%) was obtained from Aldrich, and N_2O (VLSI grade) was obtained from either Air Products or Matheson (ultrahigh purity). Suwannee River fulvic acid (SRFA) and Suwannee River humic acid (SRHA) were obtained from the International Humic Substances Society, Fluka humic acid (FHA) was obtained from Fluka Chemicals, Pony Lake and Fryxell Lake fulvic acids (PLFA, FLFA) were obtained from Dr. Y. Chin of Ohio State University, and Laurentian fulvic acid (LFA) was obtained from Fredriks Research Products.

Stock solutions of potassium ferrocyanide (0.1 M), DMA (10 mM), **I** (7 mM) DMSO (0.5 M), and fulvic and humic acids were prepared in 0.2 M borate buffer (pH 8.2), every 1−2 months. The potassium ferrocyanide stock was stored in the dark at −20 °C; other solutions were stored in the dark at 4 °C. Fluorescamine solutions (5 mM in acetonitrile) were prepared daily and stored in the dark. Natural water samples from Delaware and Chesapeake Bays were obtained either from standard Niskin bottles or the surface water pumping system aboard the *R/V Cape Henlopen*. Natural water samples from Lost Man's River, Shark River, and Caloosahatchee River were collected in a similar manner from the *R/V Walton Smith*. Surface water samples were filtered through a Gelman 0.2 μm fluted filter, whereas water from the Niskin bottles was filtered through Whatman GFF filters. These water samples were stored in the dark at 4 °C until needed and were subsequently filtered through 0.2 μm nylon filters just prior to analysis. Water used in all experiments was obtained from a Milli-Q Plus water purification system (Millipore).

Apparatus. Absorption spectra were acquired with a Hewlett-Packard 8452A diode array spectrophotometer. Monochromatic irradiations employed a GM 252 monochromator set to a band-pass of 10 nm to select light of appropriate wavelengths from the output a 1000 W Xe-Hg arc lamp powered by a 255HR power supply (Spectral Energy). Light intensities were measured using an International Light IL 1700 radiometer, calibrated by potassium ferrioxalate actinometry as previously described (*9*, *12*).

Samples were analyzed by reversed-phase high performance liquid chromatography using the system described previously (*13*). All separations were performed isocratically using a mobile phase consisting of 65% methanol and 35% sodium acetate buffer (pH 4) and a flow rate of 1 mL/min. A Hitachi L-7480 fluorescence detector set to 390 nm (excitation, 15 nm band-pass) and 490 nm (emission, 15 nm band-pass) was used for detection. Data acquisition and analysis were accomplished using ELAB software (OMS Tech Inc).

Methods

Potassium ferrocyanide (200 μM), DMSO (25 mM), and **I** (50 μM) were combined in 3 mL of 0.2 M borate buffer (pH = 8.2) within a 1-cm cuvette. Samples were first deaerated by bubbling for 10 min with either Ar or N_2 that had been passed through a O_2 trap (Alltech) and were then saturated with N_2O by bubbling for 10 min. Sample irradiation times ranged from 1 min at 296 nm to 10 min at 366 nm. A 1-mL aliquot of sample was derivatized with 300 μL of 5 mM fluorescamine; 50 μL of this derivatized sample was then injected onto the HPLC. Identical procedures were employed when 200 μM DMA was used in place of the potassium ferrocyanide, except that these samples contained 10 mM DMSO and were irradiated for 20 min at 310 nm.

To ensure quantitative scavenging of all intermediates, the dependence of the product yield (**II**) on **I** and DMSO concentration was determined as described elsewhere (*7*− *9*). Production of **II** from processes other than •OH formation via the reaction of $e^-_{(aq)}$ with N_2O was determined by conducting experiments in the absence of N_2O and/or DMSO. **II** was not observed under dark conditions.

For experiments involving the use of CH_3Cl as the probe for $e^-_{(aq)}$, samples contained 200 μM potassium ferrocyanide and 50 μM **I** at pH 8.2. After deaeration with N_2, samples were saturated with CH_3Cl by bubbling for five minutes ([CH_3-Cl] = 110 mM, ref *14*). Background levels of **II** were determined from controls irradiated in the absence of potassium ferrocyanide.

For humic substances, samples contained sufficient fulvic or humic acid to yield an initial absorbance of ∼0.1 at 296 nm, 25 mM DMSO (for SRFA the [DMSO] was 10 mM) and 50 μM **I** in the presence of borate buffer at pH 8.2. Samples were derivatized with fluorescamine and analyzed as previously described.

All natural water samples had a final volume of 3 mL and were prepared by adding 50 mM DMSO (300 μL of a 0.5 M stock solution) and 50 μM **I** (20 μM of a 7 mM stock solution) to natural water. These samples were derivatized by adding 300 μL of 5 mM fluorescamine to 1 mL of a 1:1 mixture of sample and 0.2 M borate buffer (pH = 8.2) and analyzed as previously described. For both humic substances and natural waters, irradiation times ranged between 20 and 150 min, depending on wavelength. Natural water storage times, which ranged between one and 12 months, showed no effect on $e^-_{(aq)}$ production.

Quantum yields for $e^-_{(aq)}$ formation (ϕ) were determined as the rate of methyl radical (**II**) formation per photon absorbed using the following equation:

$$\phi = \frac{RP}{0.588I_o(1 - 10^{-A})} \qquad (4)$$

where, *R* is the rate of methyl radical production (in molecules $cm^{-3} s^{-1}$), *P* is the cell path length in cm, I_o is the irradiance at the surface of the cell measured radiometrically (in photons $cm^{-2} s^{-1}$), *A* is the initial absorbance of the compound used as the source of $e^-_{(aq)}$ at the irradiation wavelength, and the factor 0.588 accounts for the difference between radiometric and actinometric measurements. Methyl radical production was determined from a calibration curve of fluorescence peak area versus concentration of **II** injected onto the HPLC; **II** was synthesized and purified using previously described procedures (*7*−*9*). For determination of ϕ's for SRFA and natural waters, the background signal due to the production of •OH from direct photolysis of CDOM (*9*) was subtracted from the sample signal. Background signals for the model compounds potassium ferrocyanide and DMA were always <5% of sample signal and therefore were not subtracted.

To test the reliability of the above procedure, relative quantum yields were also calculated using eq 5, employing previously determined quantum yields for hydroxyl radical production from nitrate and nitrite ion photolysis (*9*, *15*).

Here, ϕ_u is the quantum yield for $e^-_{(aq)}$ formation at irradiation wavelength λ, ϕ_k is the quantum yield for •OH

TABLE 1. Quantum Yields ϕ, for $e^-_{(aq)}$ Production from Potassium Ferrocyanide and N,N-Dimethylaniline

source	wavelength λ (nm)	ϕ (N$_2$O) $\times 10^2$	ϕ (CH$_3$Cl)[a] $\times 10^2$	lit value $\times 10^2$
potassium ferrocyanide (200 μM)	296	21 ± 1	22.6 ± 0.7	18 ($\lambda = $ 289 nm)[b]
potassium ferrocyanide (200 μM)	313	11.8 ± 0.1	12.0 ± 0.1	10.4[b]
potassium ferrocyanide (200 μM)	334	1.4 ± 0.1	1.49 ± 0.06	
potassium ferrocyanide (200 μM)	366	0.149 ± 0.005	0.12 ± 0.01	<2[b]
N,N-dimethylaniline (200 μM)	310	3.7 ± 0.3	ND[d]	4.0[c]

[a] Errors represent one standard deviation from mean value ($n = 3$). [b] From ref 10. [c] From ref 11. [d] ND = not determined.

$$\phi_u = \frac{\phi_k S_u A_k}{A_u S_k} \qquad (5)$$

production from nitrite or nitrate photolysis at this λ, S_k and S_u are the fluorescence peak area for **II** formed via nitrite or nitrate photolysis and $e^-_{(aq)}$ respectively, A_k is the initial absorbance value of the nitrite or nitrate solution at the irradiation wavelength and A_u is the initial absorbance of the compound used as the source of $e^-_{(aq)}$ at the irradiation wavelength. Quantum yields obtained in this fashion were within 18% of those obtained using the ferrioxalate actinometry.

Results and Discussion

Model Compounds. Irradiation of either potassium ferrocyanide or DMA in the presence of N$_2$O, DMSO, and **I** produced a significant peak eluting at approximately 10 min (Figure 1A,B) corresponding to the product previously identified as **II** (Scheme 1 and ref 7−9). This product was not observed in the absence of DMSO and N$_2$O. The small signal observed in the presence of **I** and DMSO, but absence of N$_2$O, has previously been attributed to the trace production of OH due to a minor UV-B-absorbing contaminant in **I** (9). The source of the very small amount of product formed in the presence of N$_2$O and **I**, but absence of DMSO, is unclear. Regardless, the results show that **II** arises predominantly from ·OH formed via the reaction between $e^-_{(aq)}$ and N$_2$O (Scheme 1, Figure 1).

Using 200 μM potassium ferrocyanide, an examination of the dependence of the yield of **II** on the concentration of DMSO and **I** showed that ·OH and the methyl radical were scavenged quantitatively at [DMSO] $\geq$ 25 mM and [**I**] $\geq$ 50 μM, respectively. For 200 μM DMA, these concentrations were 10 mM DMSO and 50 μM **I**, respectively. ϕ's for the photoproduction of $e^-_{(aq)}$ from potassium ferrocyanide and DMA acquired under these conditions compared reasonably with previously reported values (Table 1).

ϕ's for $e^-_{(aq)}$ production acquired with chloromethane as a probe (and employing an ·OH-independent reaction scheme) were indistinguishable from those obtained using N$_2$O, indicating that both methods provide an internally consistent and reliable measure of $e^-_{(aq)}$ production (Table 1).

Hydrated Electron Production from Humic and Fulvic Acids. Irradiation of humic and fulvic acids in the presence of N$_2$O, DMSO, and **I** also resulted in the formation of **II** (Figure 1C). Control experiments excluding N$_2$O yielded a smaller but significant amount of product with the same retention time as **II**. This background signal has previously been assigned to the direct production of ·OH by the photolysis of CDOM (9) and was subtracted from the
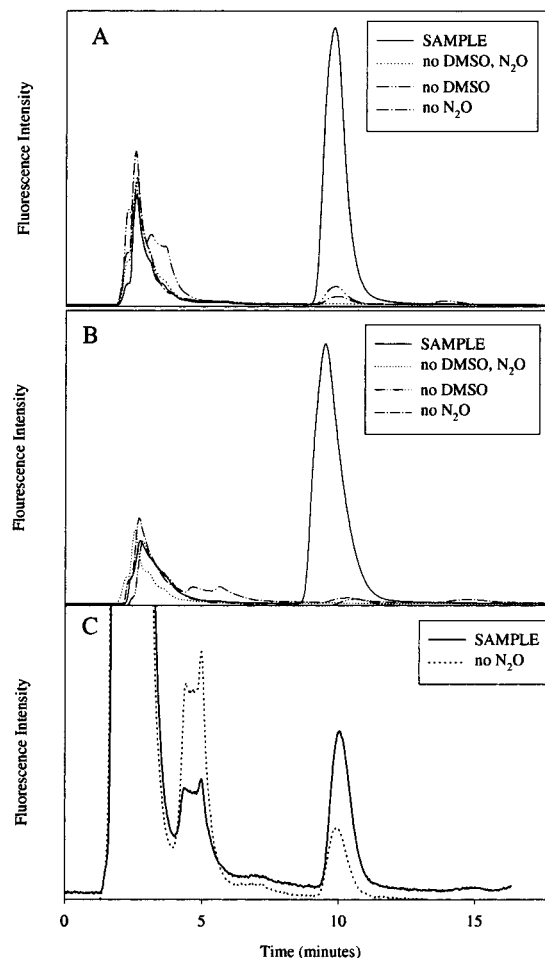

FIGURE 1. All chromatograms labeled sample were saturated with N$_2$O, contained 50 μM I, and either (A) 200 μM potassium ferrocyanide and 25 mM DMSO irradiated for 1 min at 296 nm; (B) 200 μM DMA and 10 mM DMSO irradiated for 10 min at 310 nm; or (C) 12 mg/L SRFA and 10 mM DMSO irradiated for 20 min at 296 nm. All samples were in borate buffer at pH 8.2.

fluorescence peak area of **II** acquired in the presence of N$_2$O to determine the $e^-_{(aq)}$ quantum yields.

At 296 nm, ϕ's measured for various humic and fulvic acids were very low and did not vary extensively, ranging over a factor of about two from 1.2×10^{-4} for FHA to 2.7×10^{-4} for LFA (Table 2). Surprisingly, the ϕ's decreased with increasing phenolic content of the humic substances, suggesting that phenolic moieties are not the source of $e^-_{(aq)}$. In contrast, the ϕ's were observed to increase with increasing carboxyl content, suggesting that perhaps aromatic car-

TABLE 2. Quantum Yields for e⁻$_{(aq)}$ Production from Various Humic and Fulvic Acids

sample	wave-length (nm)	phenolic content (% TOC)	carboxyl content (% TOC)	aromatic content (% TOC)	quantum yield $\times 10^4$	
					this study[a]	literature value
LFA	296	2.2[b]	33.8[b]	12.0[b]	2.7 ± 0.3	
LFA	355				0.9 ± 0.1	1600[d,e]
SRFA	296	2.55[c]	27.5[c]	28.0[c]		1.9 ± 0.2[h]
SRFA	296					1.4 ± 0.1[i]
SRFA	355				0.21 ± 0.04	0.25 ± 0.03[f,g]
						56 ± 10[e,g]
FLFA	296		19.6[j,k]	13.8[k]	1.5 ± 0.3	
PLFA	296		13.8[j,k]	12.7[k]	1.3 ± 0.3	
SRHA	296	4.93[c]	22.0[c]	42.0[c]	1.4 ± 0.1	
FHA	296				1.2 ± 0.3	<0.8[f,g]
						17 ± 2[e,g]

[a] Errors represent one standard deviation from mean value ($n = 3$). [b] From ref 26. [c] From ref 27. [d] From ref 28. [e] Laser flash photolysis. [f] Steady-state irradiation. [g] From ref 3. [h] N₂O method. [i] CH₃Cl method. [j] Carboxylic acid only. [k] From ref 29.
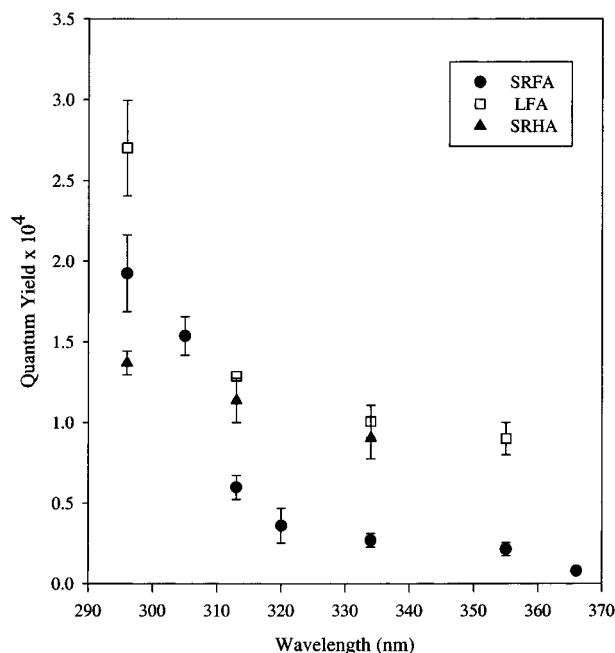

FIGURE 2. Wavelength dependence of quantum yield for hydrated electron photoproduction from SRFA (●), LFA (□), and SRHA (▲). Error bars represent one standard deviation from mean value ($n \geq 3$). Samples consist of fulvic acid (initial absorbance ~0.1 at 296 nm), 50 μM I, and 25 mM DMSO ([DMSO = 10 mM for SRFA).

boxylates, which are known to photoionize (16, 17) are the source of the e⁻$_{(aq)}$. This conclusion, however, appears to be inconsistent with the observation that there is no obvious relationship between total aromatic content and ϕ, unless the contribution of aromatic carboxylates to the total aromatic content varies between the humic substances studied.

The ϕ's for LFA, SRFA, and SRHA all decrease with increasing wavelength (Figure 2). However, the decline was more abrupt between 305 and 313 nm for SRFA as compared with SRHA and LFA. The production of e⁻$_{(aq)}$ from SRFA becomes undetectable by a wavelength of 380 nm, whereas for SRHA this occurs sooner, between 334 and 355 nm.

The value of ϕ for SRFA at 355 nm reported here (2.1 ± 0.4 $\times 10^{-5}$) agrees well with the value obtained by Zepp and co-workers (2.5 ± 0.3 $\times 10^{-5}$) using 2- chloroethanol as a probe for e⁻$_{(aq)}$ (3). However, all ϕ's determined in this study are two or more orders of magnitude lower than those obtained previously by LFP (Table 2). This discrepancy cannot
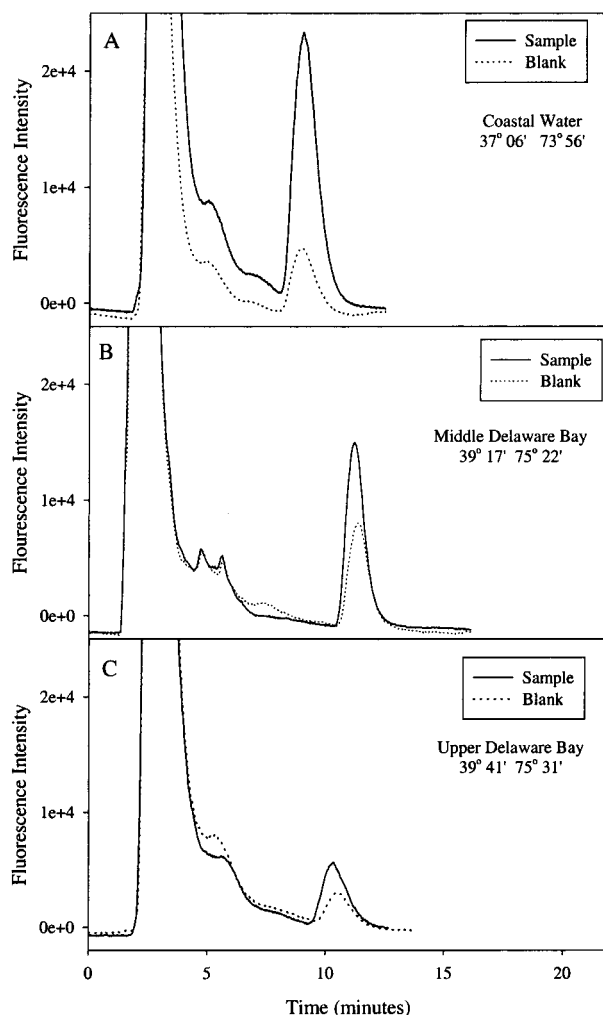
FIGURE 3. Chromatograms illustrating the formation of II from samples containing Delaware Bay or MAB water, 50 μM I and 50 mM DMSO at 296 nm. The salinity in A was 32.77 ‰, B was 19.07 ‰, and C was 4.07 ‰. Inconsistencies in retention time are due to slight differences in mobile phase composition. The formation of II was confirmed by coelution with a standard.

TABLE 3. Quantum Yields for e⁻$_{(aq)}$ Production for Waters from South Florida Rivers

sample position	location	λ (nm)	ϕ $\times 10^{4a}$	depth (m)	a[b] (m⁻¹)	salinity ‰	pH
25° 33' 81°13'	Lost Man's River	296	2.1 ± 0.5	2	23.5		8.26
25° 33' 81°13'	Lost Man's River	313	0.8 ± 0.1	2	16.2		8.26
26° 28' 82° 00'	Caloosahat-chee River	296	2.5 ± 0.7	2	6.08	29.78	7.91
25° 19' 81° 08'	Shark River	296	2.9 ± 0.7	2	12.6	34.41	7.99
25° 19' 81° 08'	Shark River	313	0.8 ± 0.1	2	9.49	34.41	7.99

[a] Errors are one standard deviation from mean value, $n = 3$. [b] $a = 2.303A/L$, where A = absorbance at irradiation wavelength and L = path length in m. All water samples were collected in June 2000.

be explained by incomplete scavenging of e⁻$_{(aq)}$ in our experiments. First, previous LFP work reported complete quenching of the transient assigned to e⁻$_{(aq)}$ under conditions of N₂O saturation as were employed in this study (2, 3). Second, given [N₂O] = 25 mM at saturation (18), hydrated electrons having lifetimes as short as ~5 ns would be scavenged; in contrast, nanosecond lifetimes for e⁻$_{(aq)}$ were never observed in the LFP experiments. These findings

TABLE 4. Quantum Yields for $e^-_{(aq)}$ Production for Waters from the Delaware Bay

sample position	location	λ (nm)	$\phi \times 10^{4a}$	depth (m)	a^b (m⁻¹)	salinity ‰	pH
39° 41 75° 31′	Upper Delaware Bay[c]	296	≤1.1[d]	2	10.6	4.07	7.68
39° 31 75° 33′	Upper Delaware Bay[c]	296	≤0.83[d]	2	9.79	9.99	7.68
39° 22′ 75° 27′	Upper Delaware Bay[c]	296	≤0.37[d]	2	7.92	15.77	7.80
39° 17′ 75° 22′	Upper-Middle Delaware Bay[c]	296	3.5 ± 0.8	13	6.40	19.07	7.44
39° 17′ 75° 22′	Upper-Middle Delaware Bay[c]	313	≤0.32[d]	13	4.63	19.07	7.44
39° 19′ 75° 24′	Upper-Middle Delaware Bay[e]	296	≤0.26[d]	2	6.23	9.01	7.58
39° 12 75° 17′	Middle Delaware Bay[e]	296	≤0.11[d]	2	4.67	15.32	7.80
39° 08′ 75° 14′	Middle Delaware Bay[e]	296	0.94 ± 0.2	2	1.63	19.24	7.65

[a] Errors are one standard deviation from mean value, $n = 3$. [b] $a = 2.303A/L$, where A = absorbance at irradiation wavelength and L = path length in m. [c] Water samples were collected in September 1998. [d] Maximum possible value determined from data that did not meet criteria for significant $e^-_{(aq)}$ production (see text). [e] Water samples were collected in October 1999.

TABLE 5. Quantum Yields for $e^-_{(aq)}$ Production for Waters from the Middle Atlantic Bight (MAB) and Chesapeake Bay

sample position	location	λ (nm)	$\phi^a \times 10^4$	depth (m)	a^b (m⁻¹)	salinity ‰	pH
38° 18′ 76° 20′	Chesapeake Bay[c]	296	3.9 ± 0.1	2	10.8	17.60	7.64
39° 05′ 76° 20′	Chesapeake Bay[c]	296	2.9 ± 0.1	2	8.05	9.85	7.64
38° 52′ 76° 24′	Chesapeake Bay[c]	296	4.11 ± 0.05	2	6.32	13.33	7.68
37° 47′ 76° 11′	Chesapeake Bay[c]	296	9.6 ± 0.1	2	5.36	19.21	7.65
39° 09′ 75° 14′	MAB[d]	296	10 ± 2	30	1.45	31.03	7.67
38° 28′ 74° 37′	MAB[d]	296	10 ± 2	12	1.56	30.43	7.91
38° 35′ 74° 46′	MAB[d]	296	24 ± 5	9	0.732	30.52	8.07
37° 06′ 73° 56′	MAB[d]	296	37 ± 4	2	0.640	32.77	8.09

[a] Errors are one standard deviation from mean value, $n = 3$. [b] $a = 2.303A/L$, where A = absorbance at irradiation wavelength and L = path length in m. [c] Water samples were collected in October 1999. [d] Water samples were collected in September 1998.

suggest that past LFP results are an artifact, perhaps of biphotonic processes, and are thus environmentally irrelevant.

Hydrated Electron Production in Natural Waters. The natural waters examined exhibited significant spatial variation in the magnitude and spectral dependence of $e^-_{(aq)}$ production. The values of ϕ at 296 nm acquired for waters from the mouths of a series of rivers draining southwest Florida were similar to each other and to SRFA. However, a more rapid decline with increasing wavelength is observed for natural waters where production of $e^-_{(aq)}$ became undetectable at a wavelength between 313 and 334 nm (Table 3).

Conversely, low- and mid-salinity waters of the upper Delaware Bay exhibit very little production of $e^-_{(aq)}$ (Table 4). Production of $e^-_{(aq)}$ was deemed to be significant if the fluorescence intensity of **II** attributable to $e^-_{(aq)}$ generation was at least twice the total standard deviation of the difference between the fluorescence intensity of **II** obtained in the presence and absence of N_2O ($n \geq 3$). The ϕ's reported in Table 4 are maximum possible values that were calculated from experimental data that did not meet this criterion.

The substantial differences observed between Upper Delaware Bay water and Florida River water, both of which should be dominated by terrestrial CDOM, cannot be explained by the differences in salinity. A mixture containing a 1:1 ratio of upper Delaware Bay water (salinity = 4 ppt) and Gulf Stream water (salinity = 36 ppt) showed no evidence of additional $e^-_{(aq)}$ production. Further, adjusting the pH to 6.7 with HCl or adding 0.5 M NaCl to Upper Delaware Bay water resulted in no additional $e^-_{(aq)}$ production. Thus, neither ionic strength nor pH can account for the differences observed for these waters.

Further evidence for spatial variability of $e^-_{(aq)}$ production was acquired in transects of the Delaware and Chesapeake Bays (Tables 4−5) and coastal waters of the Middle Atlantic Bight (MAB) (Table 5). The values of ϕ were observed to increase with increasing salinity and decreasing CDOM absorption coefficient (Tables 4−5, Figure 3), suggesting the in situ production of an $e^-_{(aq)}$ generating species. Values of

ϕ at 296 nm observed for coastal waters of the MAB were substantially larger than those measured in south Florida waters, despite the fact that CDOM absorption coefficients were lower by at least 1 order of magnitude for the MAB waters.

The results of this study thus indicate that although isolated humic substances do indeed produce $e^-_{(aq)}$ in low yield, the values of ϕ are not representative of all natural waters. The results further suggest that humic substances in natural waters may not be the principal source of $e^-_{(aq)}$ production and that other discrete UV-B absorbing chromophores, perhaps indoles (e.g., tryptophan) or aromatic carboxylic acids, are more important. These types of compounds have been shown to generate $e^-_{(aq)}$ upon photolysis (16, 17, 19), as well as being components of marine dissolved organic matter (20−22). The absence of a clear correlation of $e^-_{(aq)}$ production to CDOM absorption in marine waters, as reflected in the high degree of spatial variability of ϕ (Tables 3−5), also indicates CDOM absorption cannot be used to calculate $e^-_{(aq)}$ production rates reliably.

Contribution of Hydrated Electron to H_2O_2 Production. Comparison of quantum yields for $e^-_{(aq)}$ production obtained in this study with those reported for H_2O_2 production in natural waters at wavelengths < 313 nm (23, 24) indicate that $e^-_{(aq)}$, through the formation of superoxide, is not the primary precursor of H_2O_2 in many natural waters (Figure 4). Depending on the origin of the natural water, the contribution of $e^-_{(aq)}$ to H_2O_2 production at 296 nm ranges from 0 to 40% (Figure 4) with a higher contribution for Florida waters than Upper Delaware Bay Water. In coastal waters of the MAB where ϕ's for $e^-_{(aq)}$ are comparable to those for H_2O_2, the contribution may be as high as 100%, depending on the season (Figure 4, Table 5). However at wavelengths > 313 nm reductants aside from $e^-_{(aq)}$ appear to be principally responsible for H_2O_2 formation. These results are consistent with previous studies which report that $e^-_{(aq)}$ scavengers such as N_2O and chloroethanol have little or no effect on H_2O_2 production in natural waters (3, 25).
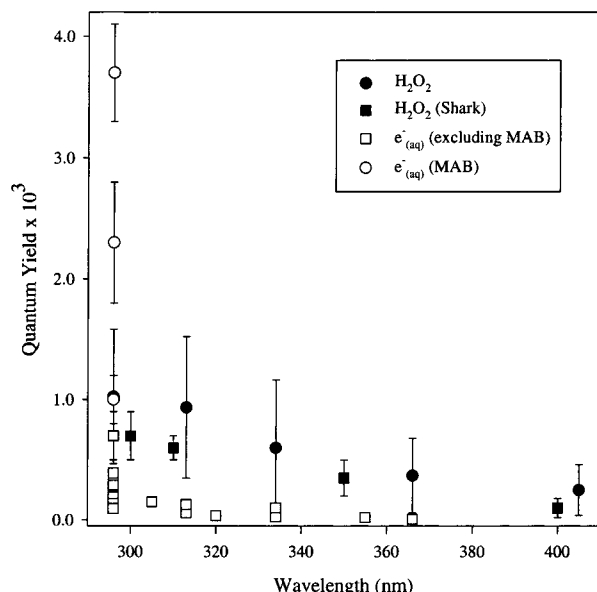
FIGURE 4. Comparison of wavelength dependence of the quantum yield for H_2O_2 production from Shark River (■), (error bars represent one standard deviation, $n = 4$; data obtained from ref 23) and other natural waters (●), (points are average values and error bars represent the range; data obtained from ref 24) to that for $e^-_{(aq)}$ production from various sources (□) (excluding MAB water) and (○) MAB water analyzed in this study.

Acknowledgments

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